

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-231235
(43)Date of publication of application : 16.08.2002

(51)Int.CI. H01M 4/24
B22F 3/02
H01M 4/26
H01M 4/62
H01M 10/30

(21)Application number : 2001-018470 (71)Applicant : SHIN ETSU CHEM CO LTD
(22)Date of filing : 26.01.2001 (72)Inventor : NAKANO TADASHI
HAMAYA NORIAKI
SHIMA SATOSHI

(54) MOLDING FOR CARBON POWDER-CONTAINING NICKEL-HYDROGEN BATTERY AND METHOD OF MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen storage alloy molding for an alkali secondary battery negative electrode and a molding electrode capable of preventing the disintegration of the molding electrode caused by charging and discharging even when a molding not including a collector support (conductive core material) is used as the electrode, ensuring the predetermined discharge capacity, and increasing a manufacturing yield in molding by using the alloy powder of a particle size of several ten μm .
SOLUTION: The hydrogen storage alloy powder, carbon colloid and a binder are mixed and granulated, and the granulated powder is pressed and molded, and then impregnated with a solution of the binder or another binder to manufacture the molding electrode.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C): 1998,2003 Japan Patent Office

*** NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The Plastic solid for nickel hydride batteries which comes to contain a hydrogen storing metal alloy and the carbon powder obtained from carbon colloid.

[Claim 2] The Plastic solid for nickel hydride batteries according to claim 1 with which the pure part of the above-mentioned carbon powder is contained 0.5 to 10% of the weight.

[Claim 3] The nickel hydride battery using the Plastic solid for nickel hydride batteries according to claim 1 or 2.

[Claim 4] The manufacture approach of the Plastic solid for nickel hydride batteries including carrying out mixing granulation of hydrogen storing metal alloy powder, carbon colloid, and the binder, and sinking the granulation powder into the solution of this binder or other binders after pressing.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] even if this invention repeats charge and discharge in more detail about a Plastic solid electrode and its manufacture approach for a long period of time -- breaking and deformation -- not happening -- again -- the inside of the electrolyte of a strong base -- alloy corrosion -- going on -- hard -- in addition -- and it is related with the hydrogen storing metal alloy which was excellent in the discharge property, the Plastic solid electrode containing carbon powder, and its manufacture approach.

[0002]

[Description of the Prior Art] Electrochemically, hydrogen storing metal alloys are occlusion and the intermetallic compound which can be made to emit, and hydrogen is mainly used as an electrode material for negative electrodes of an alkaline battery. Since it is hydrogenated in the case of charge of an electrode and dehydrogenation of this alloy is carried out in the case of discharge, it is accompanied by fluctuation of the volume at the time of charge and discharge. Therefore, in an alloy independent, the electrode destruction accompanying alloy destruction arose and utilization as an electrode was not completed. Therefore, generally, a hydrogen storing metal alloy lump is used as the powder of fixed particle size by machine grinding etc., and the electrode applied to current collection base materials, such as foaming nickel and a punching metal, is used.

[0003] The electrode structure of such a conventional type is shown in drawing 1 . In the electrode of a conventional type, the binder 3 is used for omission prevention of the hydrogen storing metal alloy powder 4 from the current collection base material 1. Moreover, in order to secure the conductivity of the hydrogen storing metal alloy powder 4 and the current collection base material 1, the electrical conducting materials 2, such as carbon and nickel powder, are added. In a water solution, the electrode of such a conventional type often kneads hydrogen storing metal alloy powder, slurs it with a binder and an electrical conducting material, and is produced by carrying out a fabricating operation to a current collection base material, after being applied and filled up.

[0004] It is effective to, make the rate that the hydrogen storing metal alloy to the whole electrode occupies increase on the other hand, in order to raise the electrode capacitance of a negative electrode. As the best approach, if an electrode is producible with a hydrogen storing metal alloy, the nickel hydrogen battery of high capacity will become producible. this invention persons produced without the current collection base material or the binder the porous body which uses and sintered [fabricated and] the hydrogen storing metal alloy powder of a specific particle size (particle diameter which is extent to which the pulverization accompanying hydrogenation and dehydrogenation does not advance to a hydrogen storing metal alloy) as the approach. Since the sintered compact of this porosity does not contain the ingredient which is not contributed to hydrogen absorption bleedoff of a current collection base material, a binder, etc., an alloy fill is high and has a high electrode capacitance consistency. However, in case such a sintered compact electrode is manufactured, the dimensional change by sintering follows. for this reason, in the electrode which needs dimensional accuracy, machine and process it -- the alloy of a part becomes useless. Therefore, it is requested that the Plastic solid without a dimensional change which does not make an alloy useless by processing is used for an electrode.

[0005] With the Plastic solid without a dimensional change, it is also requested that a predetermined electrode is produced with sufficient dimensional accuracy, and it is considered in the Plastic solid which consists only of the end of an alloy powder. By this approach, since it is necessary to hardly process it, an alloy loss is hardly generated, either. However, since the bulk density of a Plastic solid becomes lower than the bulk density of a

sintered compact when the fabricating operation of the end of an alloy powder is carried out and the Plastic solid electrode of a request is used as an electrode, the electrode capacitance consistency of an electrode falls [the part]. Here, bulk density shows volume density including the pore section of a sintered compact Plastic solid. However, countermeasures, such as using an alloy with a high alloy capacity (mAh/g) per unit weight as a means which raises the electrode capacitance consistency of a Plastic solid, or heightening a particle-size-blending method and compacting pressure, and raising pack density, are mentioned.

[0006] Moreover, the Plastic solid which does not contain a binder has a weak mechanical strength, and cannot perform necessary minimum processings (for example, fine adjustment processing of the height direction etc.). When it uses as an electrode, electrode breaking accompanying charge and discharge occurs, the alloy powder which constitutes a Plastic solid electrode drops out, and it becomes impossible moreover, to achieve the function as an electrode. As it is in JP,1-119501,A, JP,8-7891,A, JP,9-31502,A, JP,4-181655,A, and JP,59-147032,A, various examination is made [object / containing hydrogen storing metal alloy powder and a binder / pressing] about the object for hydrogen storage, or the object for alkali rechargeable battery negative electrodes. However, in case carbon powder was fabricated as the hydrogen storing metal alloy powder which pulverized particle size to dozens of micrometers, and an electric conduction agent, it was difficult for a moldability to be dramatically bad and to produce a carbon powder addition addition form electrode by the springback at the time of shaping depressuring.

[0007]

[Problem(s) to be Solved by the Invention] Even when the Plastic solid which does not contain a current collection base material (conductive core material) is used as an electrode, this invention can prevent breaking of the Plastic solid electrode by charge and discharge, and can obtain a predetermined discharge capacity, and aims at developing the high hydrogen storing metal alloy Plastic solid for alkali rechargeable battery negative electrodes of the production yield at the time of fabricating using the alloy-powder end of the particle size which is dozens of micrometers.

[0008]

[Means for Solving the Problem] this invention persons found out that this trouble is solved by being alike by using the granulation powder which kneads a binder and the carbon colloidal solution to hydrogen-storing-metal-alloy powder, and is obtained, as a result of inquiring wholeheartedly in view of the above-mentioned trouble, fabricating a porous body with predetermined bulk density, and making the opening and the alloy front face in which the above-mentioned hydrogen-storing-metal-alloy powder contacts, and they are formed distribute and contain a binder.

[0009] The hydrogen storing metal alloy Plastic solid for alkali rechargeable battery negative electrodes of this invention distributes and contains a binder on the opening and alloy front face on which the hydrogen storing metal alloy granulation powder to which carbon powder and a binder were made to adhere is contacted and formed in a hydrogen storing metal alloy powder front face, and is preferably characterized by bulk density being 3.5 - 6.0 g/cm³. Consequently, the moldability yield was good, and could prevent breaking of the Plastic solid electrode by charge and discharge, and the electrode with a high utilization factor became producible.

[0010]

[Embodiment of the Invention] First, the hydrogen storing metal alloy powder used by this invention is explained. Especially about a hydrogen storing metal alloy lump's presentation and manufacture approach of using for hydrogen storing metal alloy powder, it is not limited and ***** which has the structure of AB_n (n is the positive number of 0.5-6) and BCC-Ra Beth structure can be used.

[0011] Here, the case of AB₅ system hydrogen storing metal alloy presentation is explained to a detail as an example. In AB₅ system, the A side element is the mixture of the rare earth elements more than La independence or a kind, and La. specifically, the mixture which added other rare earth elements is mentioned to La, Mm (Mm expresses a misch metal and permutes a part of La with the rare earth elements of Ce, Pr, Nd, or others.), Lm(s) (Lm -- La -- rich -- Mm is expressed.), or such mixture. moreover, inside of rare-earth-elements mixture La -- more than 20 mol % -- containing is desirable. As a B side element, the presentation which consists of (nickel) a(Co)b(aluminum) c(Mn) d(M) e is desirable. a is the positive number of 1.8-6.0 here, and, for b, 0 or 1.0 or less positive number, and c are [0 or 1.0 or less positive number, and e of 0 or 1.0 or less positive number, and d] 0 or 0.5 or less positive number. M is a kind of element chosen from a group which consists of Si, Fe, Pb, Ti, calcium, Mg, Cu, In, Zn, Cr, and Zr at least.

[0012] After mixing each metallic element of the above-mentioned presentation, after making an alloy molten-metal-ize using a RF fusion furnace, an arc fusion furnace, etc. at the temperature of 1300-1600 degrees C, a hydrogen storing metal alloy lump is produced by cooling among the ambient atmosphere of inert gas, such as an argon. In this case, the hydrogen storing metal alloy thin band obtained by quenching methods, such as a chill roll method, and the hydrogen storing metal alloy spherical powder obtained by the disk atomizing method may be used. Moreover, you may heat-treat at the temperature in inert atmospheres, such as Ar, and around 1000 degrees C if needed.

[0013] Furthermore, a hydrogen storing metal alloy lump is ground and hydrogen storing metal alloy powder is produced. It grinds in mean particle diameter of 100 micrometers or less in inert gas ambient atmospheres, such as an argon and nitrogen gas, using a jet mill or attritor, a jaw crusher, a roller mill, a ball mill, BURAUMMIRU, etc. as the grinding approach. Or hydrogenation grinding may grind. Moreover, in the case of the hydrogen storing metal alloy spherical powder obtained by the disk atomizing method, you may use it in the state of spherical powder, and it may be further pulverized and used for the mean particle diameter of 20 micrometers or less. Moreover, after grinding, you may use it, performing surface treatment. Since the pulverization accompanying charge and discharge is remarkable and a Plastic solid may collapse if it exceeds 100 micrometers about the mean particle diameter of the hydrogen storing metal alloy powder in this case, 100 micrometers or less are desirable. Moreover, in order to control the alloy surface corrosion and capacity lowering by the strong-base electrolytic solution, 5 micrometers or more are desirable.

[0014] In this way, a binder is made to adhere to the obtained hydrogen storing metal alloy powder, it fabricates, and a hydrogen storing metal alloy Plastic solid is acquired. First, the granulation powder of the binder adhesion by hydrogen storing metal alloy powder in semi-dry process or wet granulation is prepared. Consequently, the flow nature of fine particles improves and homogeneity restoration of the fine particles to shaping metal mold is attained. Therefore, the consistency inside a Plastic solid can become homogeneity and the manufacture yield of the Plastic solid at the time of shaping can be raised.

[0015] Moreover, carbon colloid is added as an electric conduction agent at the time of granulation powder preparation. This carbon colloid distributes the carbon powder of submicron extent in a solution. Moreover, about an addition, if a carbon pure part exceeds 10 % of the weight in the last Plastic solid, the rate that the alloy powder in an electrode occupies may decrease, and an energy density may fall. Moreover, when fewer than 0.5 % of the weight in the last Plastic solid, there is no effectiveness as an electric conduction agent. Although especially the carbon particle diameter of the carbon colloid to be used is not limited, what has the particle size which is 1 micrometer - 0.01 micrometers is desirable. Moreover, although impalpable powder-like KETCHIEN black etc. is otherwise considered as a carbon electric conduction agent, since a Plastic solid collapses at the time of shaping depressuring, it cannot be used. Moreover, a globular form or a non-globular form is sufficient as the configuration of the granulation powder in this case.

[0016] Although the particle size of granulation powder is controlled with the configuration and magnitude of a Plastic solid to produce, when the pack density to a molding die is taken into consideration, it is 100-500 micrometers still more preferably 1mm or less preferably.

[0017] moreover , after knead the approach and the binder solution which be make to adhere to a front face in the end of an alloy powder , and make granulation powder to alloys , the end of an alloy powder , and carbon colloid , carry out the spray of the solution prepared so that a binder might become predetermined concentration about the method of preparation of granulation powder , the approach of evaporate a solvent and make granulation powder etc. be mention , and there be the approach of carry out fuel spray granulation using equipments , such as a spray dryer , further , and make granulation powder etc. Under the present circumstances, since a charge-and-discharge function will be spoiled if there are not much too many additions of a binder, it is not desirable. However, since the moldability of granulation powder will worsen and the Plastic solid manufacture yield will fall if too few to objection, the addition which will be contained about 0.5 to 3% of the weight in the last Plastic solid is desirable.

[0018] As a binder to be used, a water-soluble binder is desirable, for example, celluloses, such as polyvinyl alcohol, a carboxymethyl cellulose, methyl cellulose, and hydroxypropylcellulose, gelatin, a polyethylene glycol, one or more sorts of polyvinyl pyrrolidones, etc. are mentioned, and can use water, alcohol, etc. as a solvent.

[0019] A making machine is filled up so that it may become the configuration of a request of the above

granulation powder, and pressing is preferably carried out by compacting pressure 0.8 - 15 ton/cm². The Plastic solid of this invention can fabricate configurations, such as a cylinder, a prism, and telescopic, freely.

[0020] As the Plastic solid acquired by the above approach was mentioned above, although the manufacture yield improves, since it may damage in case it processes the appointed dimension or a cell can is loaded actually, since reinforcement is comparatively weak, it needs the impregnation process of a binder solution, and a desiccation process. Furthermore, in order to prevent breaking according this Plastic solid to charge and discharge, by being immersed with a binder for 0.1 to 24 hours, carrying out impregnation so that it may become 0.5 - 10% of the weight in the amount of whole about a binder into a Plastic solid, and carrying out stoving at a room temperature or room temperature -80 degree C, the pore section of a Plastic solid is adhered or filled up with a binder, and the effectiveness of the improvement in Plastic solid on the strength is acquired. [0021] This impregnation process is the approach of making a binder (solute) adhering to the alloy particle surface section which a binder water solution (solution) is fully infiltrate into the open pore section in a Plastic solid after fabricating a Plastic solid using capillarity using granulation powder, and only moisture (solvent) is evaporate after that, and faces the pore section inside a Plastic solid. Without spoiling the electric contact between alloy particles by this approach, since it becomes firm with a binder, Plastic solid reinforcement can be raised.

[0022]

[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to this.

1. The hydrogen storing metal alloy ingot (they are [% of the weight / of Nd(s) / 34 % of the weight of La(s), 45 % of the weight of Ce(s), 6 % of the weight of Pr, and / 15 / nickel] 0.20 and aluminum about 0.75 and Mn in 3.75 and Co to an atomic ratio 1.0 0.30) manufactured with the production example 1 RF fusion furnace of the Plastic solid electrode for carbon powder content nickel-hydrogen cells was heat-treated in the argon, and the uniform hydrogen storing metal alloy ingot was prepared. Coarse grinding of the alloy ingot was carried out in nitrogen-gas-atmosphere mind. Furthermore, it ground so that it might become 500 micrometers of mean diameters by BURAUMMIRU, and the raw material for jet mills was obtained. Furthermore, in this invention, dry grinding of the hydrogen storing metal alloy was carried out under gas pressure 5.8 kgf/cm² and nitrogen-gas-atmosphere mind with the jet mill, and hydrogen storing metal alloy impalpable powder with a mean particle diameter [of 15 micrometers] and a particle-size-distribution width of face of 1-100 micrometers was obtained. Next, surface treatment was carried out in 7 N-KOH which heated the ground impalpable powder, and the hydrogen storing metal alloy powder raw material was produced. Next, the solvent was evaporated, mixing said hydrogen storing metal alloy powder and carbon colloid (carbon particle diameter of about 0.8 micrometers, trade-name shadow KONDAKUTIBU colloid II: product made from the Ebara YUJI light) for the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. at a predetermined rate. Then, through granulation powder was obtained to the screen of 300 micrometers of openings. The coating weight of the polyvinyl alcohol in this case is about 0.5% of the weight of granulation powder weight. Moreover, the added carbon powder pure daily dose is 3 % of the weight. Next, metal mold with a diameter of 20mm was filled up with 1.85g of this granulation powder, and the Plastic solid with a thickness of 1mm was acquired by compacting pressure 6 ton/cm². This hydrogen storing metal alloy porosity Plastic solid was made immersed for 24 hours into the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd., it took out after that, and dried and the Plastic solid for nickel-hydrogen cell electrodes was acquired.

[0023] The solvent was evaporated mixing the carbon colloid of a predetermined rate, and the 2 % of the weight (trade name SM-4000) water solution of methyl cellulose by Shin-Etsu Chemical Co., Ltd. of a predetermined rate for the hydrogen storing metal alloy powder produced like example 2 example 1. Then, through granulation powder was obtained to the screen of 300 micrometers of openings. The coating weight of the methyl cellulose in this case is about 0.5% of the weight of granulation powder weight. Moreover, the added carbon powder pure daily dose is 8 % of the weight. Next, metal mold with a diameter of 20mm was filled up with 1.85g of this granulation powder, and the Plastic solid with a thickness of 1mm was acquired by compacting pressure 6 ton/cm². Fixed time amount immersion was carried out into the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. which dissolved this hydrogen storing metal alloy porosity Plastic solid, and it took out after that, and dried, and the Plastic solid for nickel-hydrogen cell

electrodes was acquired.

[0024] The solvent was evaporated mixing the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. of a predetermined rate for the hydrogen storing metal alloy powder produced like example of comparison 1 example 1. Then, through granulation powder was obtained to the screen of 300 micrometers of openings. The coating weight of the polyvinyl alcohol in this case is about 0.5% of the weight of granulation powder weight. Next, metal mold with a diameter of 20mm was filled up with 1.85g of this granulation powder, and the Plastic solid with a thickness of 1mm was acquired by compacting pressure 6 ton/cm². Fixed time amount immersion was carried out into the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. which dissolved this hydrogen storing metal alloy porosity Plastic solid, and it took out after that, and dried, and the Plastic solid for nickel-hydrogen cell electrodes was acquired.

[0025] The solvent was evaporated mixing the KETCHIEN black of a predetermined rate, and the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. of a predetermined rate for the hydrogen storing metal alloy powder produced like example of comparison 2 example 1. Then, through granulation powder was obtained to the screen of 300 micrometers of openings. The coating weight of the polyvinyl alcohol in this case is about 0.5% of the weight of granulation powder weight. Moreover, the added carbon powder pure daily dose is 3 % of the weight. Next, metal mold with a diameter of 20mm was filled up with 1.85g of this granulation powder, and the Plastic solid with a thickness of 1mm was acquired by compacting pressure 6 ton/cm². Fixed time amount immersion was carried out into the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. which dissolved this hydrogen storing metal alloy porosity Plastic solid, and it took out after that, and dried, and the Plastic solid for nickel-hydrogen cell electrodes was acquired.

[0026] The solvent was evaporated mixing the metal nickel powder (trade-name carbo nil nickel: product made from INCO) of a predetermined rate, and the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. of a predetermined rate for the hydrogen storing metal alloy powder produced like example of comparison 3 example 1. Then, through granulation powder was obtained to the screen of 300 micrometers of openings. The coating weight of the polyvinyl alcohol in this case is about 0.5% of the weight of granulation powder weight. Moreover, added nickel powder pure daily dose is 5 % of the weight. Next, metal mold with a diameter of 20mm was filled up with 1.85g of this granulation powder, and the Plastic solid with a thickness of 1mm was acquired by compacting pressure 6 ton/cm². Fixed time amount immersion was carried out into the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. which dissolved this hydrogen storing metal alloy porosity Plastic solid, and it took out after that, and dried, and the Plastic solid for nickel-hydrogen cell electrodes was acquired.

[0027] The solvent was evaporated mixing the carbon colloid of a predetermined rate, and the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. of a predetermined rate for the hydrogen storing metal alloy powder produced like example 3 example 1. Then, through granulation powder was obtained to the screen of 300 micrometers of openings. The coating weight of the polyvinyl alcohol in this case is about 0.5% of the weight of granulation powder weight. Moreover, the added carbon powder pure daily dose is 15 % of the weight. Next, metal mold with a diameter of 20mm was filled up with 1.85g of this granulation powder, and the Plastic solid with a thickness of 1mm was acquired by compacting pressure 6 ton/cm². Fixed time amount immersion was carried out into the 5 % of the weight (trade name C-25GP) water solution of polyvinyl alcohol by Shin-Etsu Chemical Co., Ltd. which dissolved this hydrogen storing metal alloy porosity Plastic solid, and it took out after that, and dried, and the Plastic solid for nickel-hydrogen cell electrodes was acquired.

[0028] 2. The dimension of the Plastic solid for nickel-hydrogen cell electrodes acquired in the measurement examples 1-3 of apparent density gravity and the examples 1-3 of a comparison and weight were measured, and the apparent density gravity per hydrogen storing metal alloy was computed.

[0029] 3. Compare the briquetting yield ball at the time of 20-piece production in the comparison examples 1-3 of a briquetting yield ball, and the examples 1-3 of a comparison.

[0030]

[A table 1]

| | 造粒バインダー 種類と添加量 | 導電剤 種類と添加量 | 見掛け密度 (g/cm ³) | 成形歩留 (%) |
|-------|-------------------|----------------|-------------------------------|-------------|
| 実施例 1 | PVA 0.5重量% | カーボンコロイド 3重量% | 5.56 | 65 |
| 実施例 2 | MC 0.5重量% | カーボンコロイド 8重量% | 5.31 | 60 |
| 比較例 1 | PVA 0.5重量% | なし | 5.48 | 80 |
| 比較例 2 | PVA 0.5重量% | ケッテンフーラック 3重量% | - | 0 |
| 比較例 3 | PVA 0.5重量% | ニッケル粉末 5重量% | 5.51 | 70 |
| 実施例 3 | PVA 0.5重量% | カーボンコロイド 15重量% | 5.01 | 30 |

[0031] The briquetting yield by the crack of a thin Plastic solid with a thickness [in a forming cycle] of 1mm is shown in a table 1. By the springback at the time of shaping depressuring, since it cannot fabricate, the yield of the granulation powder which mixed KETCHIEN black is very as bad as 0%. On the other hand, when it added as carbon colloid, it was checked that it can fabricate also with the same carbon powder. However, in the case of the example 3 with many additions, apparent density has fallen remarkably and it turns out that the capacity per volume of an electrode (energy density) is low.

[0032] 4. In the charge-and-discharge property measurement examples 1-3 by the negative-electrode regulation open sand mold cell, and the examples 1-3 of a comparison, the Plastic solid was cut down in the dimension of cm (10x10)2, and it put with the felt made from nickel as a charge collector, and wrapped in the network made from nickel (100 meshes of aperture sizes) after that, and nickel lead was welded, and it wrapped in the nonwoven fabric made from polypropylene after that, and considered as the negative electrode. Capacity is equivalent to about 150 mAh/g for the alloy weight in this case by about 0.5g. On the other hand, the positive electrode used two sintering type nickel hydroxide poles (50x50) cm² produced by well-known technique. The electrolytic solution performed the charge and discharge test using 6 N-KOH, using a Hg/HgO pole as a reference pole. Charge-and-discharge conditions are made to discharge, after charging for 7.5 hours and leaving it after that in 60mA per alloy weight under the constant temperature of 25 degrees C for 30 minutes until they are set to 0.65V to a Hg/HgO pole by 60mA per alloy weight. 100 cycle charge and discharge were repeated on this condition. Moreover, it was made to discharge until it was set to 0.50V to the Hg/HgO pole by 300mA per alloy weight during this cycle trial, and high-rate-discharge weighted solidity was compared. The result is shown in a table 2.

[0033]

[A table 2]

| | バインダー 種類と添加量 | 導電剤 種類と添加量 | 1サイクル目 容量(mAh/g) | 10サイクル目 容量(mAh/g) | 100サイクル目 容量(mAh/g) | 高率放電 容量(mAh/g) |
|-------|-----------------|-------------------|---------------------|----------------------|-----------------------|-------------------|
| 実施例 1 | PVA 0.5重量% | カーボンコロイド 3重量% | 278 | 299 | 280 | 275 |
| 実施例 2 | MC 0.5重量% | カーボンコロイド 8重量% | 285 | 298 | 280 | 275 |
| 比較例 1 | PVA 0.5重量% | なし | 268 | 281 | 240 | 230 |
| 比較例 2 | PVA 0.5重量% | ケッテンフーラック 3重量% | - | - | - | - |
| 比較例 3 | PVA 0.5重量% | ニッケル粉末 5重量% | 279 | 288 | 269 | 282 |
| 実施例 3 | PVA 0.5重量% | カーボンコロイド 15重量% | 270 | 278 | 233 | 281 |

[0034] From the result of a charge and discharge test, the examples 1 and 2 of capacity [the attainment capacity and high-rate-discharge capacity] of 10 cycle eye which mixed carbon colloid are improving compared with the example 1 of a comparison without an electric conduction agent, and the example 3 of a comparison using nickel powder as an electric conduction agent. Since conductivity is good, this is considered because the utilization factor of an electrode became good. However, in the case of an example 3, since the carbon powder which carried out abundant content of the carbon powder of low specific gravity, and a moldability was not

good and added cannot function as an electric conduction agent, attainment capacity is also low. Moreover, since the moldability is bad, capacity lowering according to omission of an alloy grain etc. by the charge and discharge of a repeat is also large. On the other hand, as it was also the comparison of the shaping yield, since it was not able to fabricate, the example 2 of a comparison which added the powder of KETCHIEN black as an electric conduction agent was not able to measure the property as an electrode.

[0035]

[Effect of the Invention] The carbon powder addition for raising the conductivity of a Plastic solid electrode by this invention as mentioned above is attained, and a high-rate-discharge property can offer the good Plastic solid for nickel-hydrogen cells.

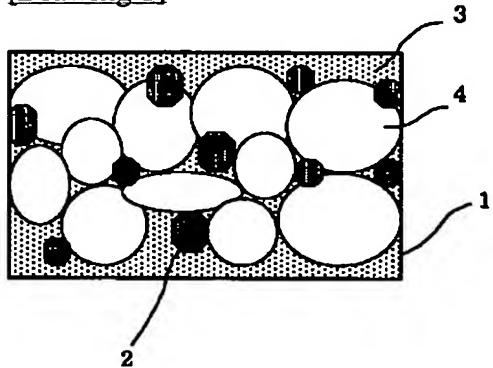
[Translation done.]

* NOTICES *

**JPO and NCIP are not responsible for any
damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

[Translation done.]

(19)日本国特許庁 (JP)

(12)公開特許公報 (A)

(11)特許出願公開番号

特開2002-231235

(P 2 0 0 2 - 2 3 1 2 3 5 A)

(43)公開日 平成14年8月16日 (2002.8.16)

| (51) Int. Cl. ⁷ | 識別記号 | F I | マーク* (参考) |
|----------------------------|-------|-----------------|------------|
| H 01 M | 4/24 | H 01 M | 4/24 |
| B 22 F | 3/02 | B 22 F | 3/02 |
| H 01 M | 4/26 | H 01 M | 4/26 |
| | 4/62 | | 4/62 |
| | 10/30 | | 10/30 |
| | | | Z |
| | | 審査請求 未請求 請求項の数4 | OL (全 6 頁) |

| | | | |
|----------|----------------------------|---------|---|
| (21)出願番号 | 特願2001-18470 (P2001-18470) | (71)出願人 | 000002060 信越化学工業株式会社 東京都千代田区大手町二丁目6番1号 |
| (22)出願日 | 平成13年1月26日 (2001.1.26) | (72)発明者 | 中野 端 福井県武生市北府二丁目1番5号 信越化学 工業株式会社磁性材料研究所内 |
| | | (72)発明者 | 浜谷 典明 福井県武生市北府二丁目1番5号 信越化学 工業株式会社磁性材料研究所内 |
| | | (74)代理人 | 100099623 弁理士 奥山 尚一 (外3名) |
| | | | 最終頁に続く |

(54)【発明の名称】カーボン粉含有ニッケルー水素電池用成形体及びその製造方法

(57)【要約】

【課題】集電支持体(導電性芯材)を含有しない成形体を電極として用いた場合でも、充放電による成形体電極の崩壊を防止することができ、かつ所定の放電容量を得ることができ、数十 μ mの粒径の合金粉末を用いて成形する際の作製歩留まりの高いアルカリ二次電池負極用水素吸蔵合金成形体及び成形体電極を開発する。

【解決手段】水素吸蔵合金粉末とカーボンコロイドとバインダーを混合造粒し、その造粒粉を加圧成形後、該バインダー又は他のバインダーの溶液に含浸して成形体電極を得る。

10/11

| |
|---------------|
| JP03-0354 |
| -00W0-TD |
| 04.1.27 |
| SEARCH REPORT |

【特許請求の範囲】

【請求項1】 水素吸蔵合金と、カーボンコロイドから得られるカーボン粉を含んでなるニッケルー水素電池用成形体。

【請求項2】 上記カーボン粉の純分が、0.5~1.0重量%含まれる請求項1に記載のニッケルー水素電池用成形体。

【請求項3】 請求項1又は請求項2に記載のニッケルー水素電池用成形体を用いたニッケルー水素電池。

【請求項4】 水素吸蔵合金粉末とカーボンコロイドとバインダーを混合造粒し、その造粒粉を加圧成形後、該バインダー又は他のバインダーの溶液に含浸することを含むニッケルー水素電池用成形体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、成形体電極及びその製造方法に関し、さらに詳しくは長期間充放電を繰り返しても崩壊、変形が起こらずまた、強アルカリの電解質中でも合金腐食が進行しづらく、なお且つ放電特性の優れた水素吸蔵合金とカーボン粉を含む成形体電極とその製造方法に関する。

【0002】

【従来の技術】 水素吸蔵合金は、電気化学的に水素を吸蔵・放出させることができる金属間化合物であり、主にアルカリ蓄電池の負極用電極材料として利用されている。この合金は、電極の充電の際に水素化され、放電の際に脱水素化されるため、充放電時に体積の変動を伴う。そのため合金単独では合金破壊に伴う電極破壊が生じて、電極としての利用ができなかった。したがって、一般的には、水素吸蔵合金塊を機械粉碎等により一定粒径の粉末にし、発泡ニッケルやパンチングメタルなどの集電支持体に塗布した電極が利用されている。

【0003】 このような従来型の電極構造を図1に示す。従来型の電極では、集電支持体1からの水素吸蔵合金粉末4の脱落防止のためにバインダー3を使用している。また、水素吸蔵合金粉末4と集電支持体1との導電性を確保するためにカーボンやニッケル粉などの導電材料2を添加している。このような従来型の電極は、水素吸蔵合金粉末を水溶液中でバインダー及び導電材料と共に混練してスラリー化し、集電支持体に塗布・充填した後、成形加工することによって作製されている。

【0004】 一方、負極の電極容量を高めるためには、電極全体に対する水素吸蔵合金の占める割合を増加させることができが効果的である。最善の方法としては、水素吸蔵合金のみで電極を作製することができれば、高容量のニッケル水素蓄電池が作製可能となる。本発明者らは、その方法として、集電支持体やバインダーなしで、特定の粒径（水素吸蔵合金に水素化、脱水素化に伴う微粉化が進行しない程度の粒子径）の水素吸蔵合金粉末を用いて成形、焼結した多孔質体を作製した。この多孔質の焼結

体は、集電支持体やバインダー等の水素吸蔵放出に寄与しない材料を含まないため、合金充填量が高く、高電極容量密度を有する。しかし、このような焼結体電極を製造する際には、焼結による寸法変化が伴う。このため寸法精度の必要な電極等では、機械加工を施さなければならず、加工しろ分の合金が無駄になる。したがって、加工によって合金を無駄にしない、寸法変化のない成形体を電極に使用することが要望されている。

【0005】 寸法変化のない成形体では、所定の電極を寸法精度良く作製することも要望されて、合金粉末のみからなる成形体が考えられている。この方法では加工をほとんど施さなくてもよいため、合金ロスもほとんど発生しない。しかし、合金粉末を成形加工したのみの成形体電極は、電極として用いた場合、成形体の嵩密度が焼結体の嵩密度より低くなるため、その分だけ電極の電極容量密度が低下する。ここで、嵩密度とは、焼結体成形体の気孔部を含めた体積密度を示す。但し、成形体の電極容量密度を高める手段として、単位重量あたりの合金容量 (mA h/g) の高い合金を用いることや、粒度配合法、成形圧力を高めて充填密度を上げることなどの対応策が挙げられる。

【0006】 また、バインダーを含有しない成形体は、機械的強度が弱く、必要最小限の加工（たとえば高さ方向の微調整加工など）ができない。また、電極として用いた際、充放電に伴う電極崩壊が発生し、成形体電極を構成する合金粉が脱落し、電極としての機能が果たせなくなる。水素吸蔵合金粉末とバインダーを含有する加圧成形体については、特開平1-119501号公報、特開平8-7891号公報、特開平9-31502号公報、特開平4-181655号公報、特開昭59-147032号公報にあるように、水素貯蔵用やアルカリ二次電池負極用について種々の検討がなされている。しかし、粒径を数十 μ mに微粉碎した水素吸蔵合金粉末と導電剤としてカーボン粉末を成形する際、成形脱圧時のスプリングバックによって成形性が非常に悪く、カーボン粉添加成形体電極を作製することが困難であった。

【0007】

【発明が解決しようとする課題】 本発明は、集電支持体（導電性芯材）を含有しない成形体を電極として用いた場合でも、充放電による成形体電極の崩壊を防止することができ、かつ所定の放電容量を得ることができ、数十 μ mの粒径の合金粉末を用いて成形する際の作製歩留まりの高いアルカリ二次電池負極用水素吸蔵合金成形体を開発することを目的とする。

【0008】

【課題を解決するための手段】 本発明者らは、上記問題点に鑑み鋭意研究を行った結果、水素吸蔵合金粉末にバインダーとカーボンコロイド溶液を混練して得られる造粒粉を用いることによりに所定の嵩密度を有す多孔質体を成形し、上記水素吸蔵合金粉末同士が接触して形成さ

れる空隙及び合金表面にバインダーを分散して含有させることによって、かかる問題点が解決されることを見出した。

【0009】本発明のアルカリ二次電池負極用水素吸蔵合金成形体は、水素吸蔵合金粉末表面にカーボン粉末およびバインダーを付着させた水素吸蔵合金造粒粉が接触して形成される空隙及び合金表面にバインダーを分散して含有し、好ましくは、嵩密度が3.5～6.0 g/cm³であることを特徴とする。その結果、成形性歩留まりが良く、充放電による成形体電極の崩壊を防止でき、かつ利用率の高い電極が作製可能になった。

【0010】

【発明の実施の形態】先ず、本発明で用いる水素吸蔵合金粉末について説明する。水素吸蔵合金粉末に用いる水素吸蔵合金塊の組成および製造方法については、特に限定されるものではなく、AB_n (nは0.5～6の正数)の構造やBCC-ラーベス構造を有する水素吸蔵合金やを使用することができる。

【0011】ここでは例として、AB_n系水素吸蔵合金組成の場合について詳細に説明する。AB_n系において、A側元素は、La単独、または一種以上の希土類元素とLaとの混合物である。具体的には、La、Mm (Mmは、ミッシュメタルを表し、Laの一部をCe、Pr、Nd又はその他の希土類元素で置換したものである。)、Lm (Lmは、LaリッチMmを表す。)、又はこれらの混合物に他の希土類元素を添加した混合物が挙げられる。また、希土類元素混合物中にLaを20モル%以上含むことが好ましい。B側元素としては、(Ni)、(Co)、(Al)、(Mn)、(M)からなる組成が好ましい。ここでaは1.8～6.0の正数であり、bは0または1.0以下の正数、cは0または1.0以下の正数、dは0または1.0以下の正数、eは0または0.5以下の正数である。Mは、Si、Fe、Pb、Ti、Ca、Mg、Cu、In、Zn、Cr及びZrからなる一群から選ばれた少なくとも一種の元素である。

【0012】上記組成の各金属元素を混合した後、アルゴン等の不活性ガスの雰囲気中、1300～1600℃の温度で高周波溶解炉やアーク溶解炉等を用いて合金を溶湯化させた後、冷却することによって水素吸蔵合金塊を作製する。この場合、ロール急冷法等の急冷法により得られた水素吸蔵合金薄帯、ディスクアトマイズ法により得られた水素吸蔵合金球状粉を用いてもよい。また必要に応じてAr等の不活性雰囲気中、1000℃前後の温度で熱処理を行っても良い。

【0013】さらに、水素吸蔵合金塊を粉碎して水素吸蔵合金粉末を作製する。粉碎方法としては、ジェットミル又はアトライター、ジョークラッシャー、ローラーミル、ボールミル、ブラウンミル等を用いてアルゴンや窒素ガス等の不活性ガス雰囲気中で平均粒径100μm以下に粉碎する。あるいは、水素化粉碎により粉碎しても

よい。また、ディスクアトマイズ法により得られた水素吸蔵合金球状粉の場合は球状粉の状態で使用しても良いし、さらに平均粒径20μm以下に粉碎して使用しても良い。また、粉碎した後に表面処理を施して使用してもよい。この場合の水素吸蔵合金粉末の平均粒径については100μmを超えると充放電に伴う微粉化が著しく成形体が崩壊してしまう場合があるため100μm以下が好ましい。また、強アルカリ電解液による合金表面腐食・容量低下を抑制するため5μm以上が好ましい。

10 【0014】こうして得られた水素吸蔵合金粉にバインダーを付着させて成形して水素吸蔵合金成形体を得る。先ず、水素吸蔵合金粉末を半乾式あるいは湿式造粒法にてバインダー付着の造粒粉を調製する。その結果、粉体の流れ性が向上し成形金型への粉体の均一充填が可能になる。そのため成形体内部の密度が均一になり成形時の成形体の製造歩留まりを向上させることが出来る。

【0015】また、造粒粉調製時に導電剤としてカーボンコロイドを添加する。このカーボンコロイドは溶液中にサブミクロン程度のカーボン粉末を分散させたものである。また、添加量については、カーボン純分が最終の成形体中の10重量%を超えると電極中の合金粉の占める割合が減りエネルギー密度が低下してしまう場合がある。また、最終の成形体中の0.5重量%より少ないと導電剤としての効果がない。用いるカーボンコロイドのカーボン粒子径は特に限定しないが1μm～0.01μmの粒径を有するもののが好ましい。また、カーボン導電剤としては他に微粉末状のケッテンブラック等も考えられるが成形脱圧時に成形体が崩壊してしまうため使用できない。また、この場合の造粒粉の形状は球形でも非球形でもよい。

【0016】造粒粉の粒径は作製する成形体の形状や大きさによってコントロールするが、成形用金型への充填密度を考慮すると、好ましくは1mm以下、更に好ましくは100～500μmである。

【0017】また、造粒粉の調製法についてはバインダーが所定の濃度になるように調製した溶液をスプレーしながら合金粉末表面に付着させて合金同士を造粒粉に仕上げる方法やバインダー溶液と合金粉末とカーボンコロイドを混練した後、溶媒を蒸発させ造粒粉に仕上げる方法などが挙げられ、さらにはスプレードライヤー等の装置を用いて噴霧造粒して造粒粉に仕上げる方法などがある。この際、バインダーの添加量があり多すぎると充放電機能が損なわれるため好ましくない。しかし、反対に少なすぎると造粒粉の成形性が悪くなり成形体製造歩留まりが低下するため、最終の成形体中に0.5～3重量%程度含まれることとなる添加量が好ましい。

【0018】用いるバインダーとしては、水溶性バインダーが好ましく、例えば、ポリビニルアルコール、カルボキシメチルセルロース、メチルセルロース、ヒドロキシプロピルセルロース等のセルロース類、ゼラチン、ポ

リエチレングリコール、ポリビニルピロリドン等が1種以上挙げられ、溶媒としては、水、アルコール等を使用することができる。

【0019】上記のような造粒粉を所望の形状になるように成形機に充填し、好ましくは、成形圧力0.8~1.5ton/cm²で加圧成形する。本発明の成形体は円柱、角柱、筒型等の形状を自由に成形することができる。

【0020】以上的方法で得られた成形体は、上述したように製造歩留まりは向上するものの強度は比較的弱いため指定の寸法に加工したり実際に電池缶に装填する際に破損してしまう可能性があるため、バインダー溶液の含浸工程、乾燥工程を必要とする。さらに、該成形体を充放電による崩壊を防止するために、バインダーにて0.1~2.4時間浸漬して、成形体中にバインダーを全体量で0.5~1.0重量%になるように含浸させ、室温又は室温~80℃で加熱乾燥させることにより、成形体の気孔部にバインダーが付着、または充填され成形体強度向上といった効果が得られるものである。

【0021】この含浸工程は、造粒粉を用いて成形体を成形後、毛細管現象を利用して成形体中の開気孔部にバインダー水溶液（溶液）を充分に染み込ませ、その後に水分（溶媒）のみを蒸発させて成形体内部の気孔部に面する合金粒子表面部にバインダー（溶質）を付着させる方法である。この方法により合金粒子間の電気的コンタクトが損なわれることなく、バインダーによって強固になるため成形体強度を高めることが出来る。

【0022】

【実施例】以下、本発明を実施例により更に詳細に説明するが、本発明はこれに限定されるものではない。

1. カーボン粉含有Ni—水素電池用成形体電極の作製実施例1

高周波溶解炉にて製造された水素吸蔵合金インゴット（La34重量%、Ce45重量%、Pr6重量%、Nd15重量%を原子比1.0に対し、Niを3.75、Coを0.75、Mnを0.20、Alを0.30）をアルゴン中で熱処理し、均一な水素吸蔵合金インゴットを準備した。その合金インゴットを窒素雰囲気中で粗粉碎した。更に、ブラウンミルで平均粒径500μmになるように粉碎し、ジェットミル用の原料を得た。更に本発明では、ジェットミルによりガス圧5.8kgf/cm²、窒素ガス雰囲気下で水素吸蔵合金を乾式粉碎し、平均粒径15μm、粒度分布幅1~100μmの水素吸蔵合金微粉末を得た。次に粉碎された微粉末を加熱した7N-KOH中で表面処理し水素吸蔵合金粉末原料を作製した。次に、信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液を所定の割合で前記水素吸蔵合金粉末およびカーボンコロイド（カーボン粒子径約0.8μm、商品名シャドーコンダクティブコロイドII：荏原ユージライト製）とを混合しながら溶媒を蒸発させた。その後、目開き300μmの篩に通し

造粒粉を得た。この場合のポリビニルアルコールの付着量は造粒粉重量の約0.5重量%である。また、添加したカーボン粉末純分量は3重量%である。次に、この造粒粉1.85gを直径20mmの金型に充填し成形圧力6ton/cm²で厚さ1mmの成形体を得た。この水素吸蔵合金多孔質成形体を信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液中に24時間浸漬させ、その後取り出して乾燥しNi—水素電池電極用成形体を得た。

10 【0023】実施例2

実施例1と同様にして作製した水素吸蔵合金粉末を所定の割合のカーボンコロイドと所定の割合の信越化学工業社製のメチルセルロース（商品名SM-4000）2重量%水溶液とを混合しながら溶媒を蒸発させた。その後、目開き300μmの篩に通し造粒粉を得た。この場合のメチルセルロースの付着量は造粒粉重量の約0.5重量%である。また、添加したカーボン粉末純分量は8重量%である。次に、この造粒粉1.85gを直径20mmの金型に充填し成形圧力6ton/cm²で厚さ1mmの成形体を得た。

20 【0024】比較例1

実施例1と同様にして作製した水素吸蔵合金粉末を所定の割合の信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液とを混合しながら溶媒を蒸発させた。その後、目開き300μmの篩に通し

30 造粒粉を得た。この場合のポリビニルアルコールの付着量は造粒粉重量の約0.5重量%である。次に、この造粒粉1.85gを直径20mmの金型に充填し成形圧力6ton/cm²で厚さ1mmの成形体を得た。この水素吸蔵合金多孔質成形体を溶解した信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液中に一定時間浸漬させ、その後取り出して乾燥しNi—水素電池電極用成形体を得た。

【0025】比較例2

実施例1と同様にして作製した水素吸蔵合金粉末を所定の割合のケッテンブラックと所定の割合の信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液とを混合しながら溶媒を蒸発させた。その後、目開き300μmの篩に通し造粒粉を得た。この場合のポリビニルアルコールの付着量は造粒粉重量の約0.5重量%である。また、添加したカーボン粉末純分量は3重量%である。次に、この造粒粉1.85gを直径20mmの金型に充填し成形圧力6ton/cm²で厚さ1mmの成形体を得た。この水素吸蔵合金多孔質成形体を溶解した信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液中に一定時間浸漬さ

せ、その後取り出して乾燥しN i - 水素電池電極用成形体を得た。

【0026】比較例3

実施例1と同様にして作製した水素吸蔵合金粉末を所定の割合の金属N i 粉末（商品名カーボニルニッケル：I NCO製）と所定の割合の信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液とを混合しながら溶媒を蒸発させた。その後、目開き300μmの篩に通し造粒粉を得た。この場合のポリビニルアルコールの付着量は造粒粉重量の約0.5重量%である。また、添加したN i 粉末純分量は5重量%である。次に、この造粒粉1.85gを直径20mmの金型に充填し成形圧力6ton/cm²で厚さ1mmの成形体を得た。この水素吸蔵合金多孔質成形体を溶解した信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液中に一定時間浸漬させ、その後取り出して乾燥しN i - 水素電池電極用成形体を得た。

【0027】実施例3

実施例1と同様にして作製した水素吸蔵合金粉末を所定の割合のカーボンコロイドと所定の割合の信越化学工業社製のポリビニルアルコール（商品名C-25GP）5

重量%水溶液とを混合しながら溶媒を蒸発させた。その後、目開き300μmの篩に通し造粒粉を得た。この場合のポリビニルアルコールの付着量は造粒粉重量の約0.5重量%である。また、添加したカーボン粉末純分量は1.5重量%である。次に、この造粒粉1.85gを直径20mmの金型に充填し成形圧力6ton/cm²で厚さ1mmの成形体を得た。この水素吸蔵合金多孔質成形体を溶解した信越化学工業社製のポリビニルアルコール（商品名C-25GP）5重量%水溶液中に一定時間浸漬させ、その後取り出して乾燥しN i - 水素電池電極用成形体を得た。

【0028】2. 見かけ密度の測定

実施例1～3、比較例1～3で得られたN i - 水素電池電極用成形体の寸法、重量を測定し、水素吸蔵合金当たりの見かけ密度を算出した。

【0029】3. 成形歩留まりの比較

実施例1～3、比較例1～3において20ヶ作製時の成形歩留まりを比較する。

【0030】

20 【表1】

| | 造粒バインダー 種類と添加量 | 導電材 種類と添加量 | 見掛け密度 (g/cm ³) | 成形歩留 (%) |
|------|-------------------|---------------|-------------------------------|-------------|
| 実施例1 | PVA0.5重量% | カーボンコロイド3重量% | 5.56 | 65 |
| 実施例2 | MC0.5重量% | カーボンコロイド8重量% | 5.31 | 60 |
| 比較例1 | PVA0.5重量% | なし | 5.46 | 60 |
| 比較例2 | PVA0.5重量% | カーボンコロイド3重量% | - | 0 |
| 比較例3 | PVA0.5重量% | カーボン粉末5重量% | 5.51 | 70 |
| 実施例3 | PVA0.5重量% | カーボンコロイド15重量% | 5.01 | 30 |

【0031】表1に成形工程における厚み1mmの薄型成形体のクラックによる成形歩留を示す。ケッテンブランクを混合した造粒粉は成形脱圧時のスプリングバックによって成形が不可能であるため歩留りは0%と極めて悪い。一方、カーボンコロイドとして添加した場合、同じカーボン粉末でも成形が可能であることが確認された。しかし、添加量の多い実施例3の場合、見掛け密度が著しく低下してしまっており電極の体積当りの容量（エネルギー密度）が低いことがわかる。

【0032】4. 負極規制開放型電池による充放電特性測定

実施例1～3、比較例1～3において(10×10)cm²の寸法に成形体を切り出し集電体としてN i 製のフェルトで挟み込み、その後N i 製の網（目開100メッシュ）で包み込みN i リードを溶接し、その後ポリプロ

ピレン製の不織布で包み込み負極とした。この場合の合金重量は約0.5gで容量は約150mA h/gに相当する。一方、正極は公知の手法で作製された焼結式水酸化ニッケル極(50×50)cm²を2枚用いた。電解液は6N-KOHを用い参照極としてHg/HgO極を用い充放電試験を行なった。充放電条件は25℃の一定温度下で合金重量当り60mAで7.5時間充電しその後30分放置した後、合金重量当り60mAでHg/HgO極に対し0.65Vとなるまで放電させる。この条件で100サイクル充放電を繰り返した。また、このサイクル試験中に合金重量当り300mAでHg/HgO極に対し0.50Vとなるまで放電させ高率放電特性値を比較した。その結果を表2に示す。

【0033】

【表2】

| 実施例 | バインダー 種類と添加量 % | 導電剤 種類と添加量 % | 充電容量 (mAh/g) | | 高率放電 容量 (mAh/g) | |
|-------|----------------------|--------------------|--------------|---------|--------------------|------------|
| | | | 100%目 | 100%95目 | 100%75目 | 容量 (mAh/g) |
| 実施例 1 | PVA 0.5重量% | ケーブンコロイド 3重量% | 278 | 299 | 280 | 275 |
| 実施例 2 | NC 0.5重量% | ケーブンコロイド 3重量% | 285 | 298 | 290 | 275 |
| 比較例 1 | PVA 0.5重量% | なし | 258 | 281 | 240 | 230 |
| 比較例 2 | PVA 0.5重量% | ケブンブラック 3重量% | - | - | - | - |
| 比較例 3 | PVA 0.5重量% | コバル粉末 5重量% | 279 | 269 | 263 | 262 |
| 実施例 3 | PVA 0.5重量% | ケーブンコロイド 15重量% | 270 | 278 | 233 | 251 |

【0034】充放電試験の結果から、カーボンコロイドを混合した実施例1、2は導電剤なしの比較例1、導電剤としてNi粉末を用いた比較例3に比べて10サイクル目の到達容量及び高率放電容量とともに向上している。これは導電性が良好であるため電極の利用率が良くなつたためと考えられる。しかし、実施例3の場合は低比重のカーボン粉を多量含有して成形性が良好でなく添加したカーボン粉が導電剤として機能しきれていないため到達容量も低い。また、成形性が悪いため繰り返しの充放電により合金粒の脱落等による容量低下も大きい。一方、導電剤としてケブンブラックの粉末を添加した比較例2は成形歩留りの比較でもあったように成形が不可能なため電極としての特性は測定できなかった。

【0035】

【発明の効果】以上のように本発明により成形体電極の導電性を向上させるためのカーボン粉添加が可能になり、高率放電特性が良好なNi—水素電池用成形体を提供できる。

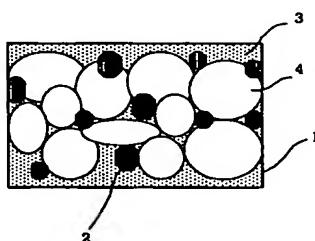
【図面の簡単な説明】

【図1】従来型の電極構造を示す。

【符号の説明】

20 1 集電支持体 (導電芯体)
2 導電剤
3 バインダー及び空孔
4 水素吸蔵合金粉末

【図1】



フロントページの続き

(72)発明者 島 聰
福井県武生市北府二丁目1番5号 信越化
学工業株式会社磁性材料研究所内

F ターム(参考) 4K018 CA08 KA38
5H028 BB03 BB04 BB06 EE01 EE06
EE08 HH01
5H050 AA19 BA14 CA03 CB16 DA03
DA10 DA11 EA08 EA23 GA03
GA06 GA08 GA10 GA23 HA01

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.